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## SEMIEMPIRICAL ENERGIES OF VACANCY FORMATION IN SEMICONDUCTORS

*Using the extended Hückel method and the methods based on thermochemical, thermodynamic, and electrophysical data, the energies of vacancy formation in  $A^{II}B^{VI}$ ,  $A^{III}B^V$ , and  $A^{IV}B^{VI}$  semiconductor crystals have been determined. A correlation of the obtained values with one another and with the literature experimental and ab initio theoretical data is established. This testifies to the adequacy of the applied methods and to a possibility of using them for the estimation of the defect concentration in semiconductors.*

*Keywords:* semiconductors, point defects, defect formation energy.

### 1. Introduction

The importance of researches dealing with the defect subsystem in semiconductor materials is associated with a considerable influence of the type of structural disordering on the whole complex of the physico-chemical properties of crystals. The main, from the viewpoint of practical applications, properties of semiconductor crystals – such as optical, electric, and thermodynamic ones – are the most sensitive to point (or zero-dimensional) defects. The latter arise as a result of the violation in the periodicity of atomic arrangement. Their presence in the lattice is connected with the crystal nonstoichiometry and other factors. Detailed information about the type and the concentration of point defects, as well as the factors affecting them, makes it possible to control the defect subsystem of a semiconductor and, hence, its physico-chemical properties [1–3].

The development level of modern experimental techniques does not allow yet the concentration of point defects to be directly calculated, especially in the cases where the crystal contains defects of different types (vacancies, interstitial atoms, or their complexes), so that the measured crystal parameters are a result of their cumulative action. Therefore, theoretical methods have to be applied in order to calculate the point defect concentration. In this case, the problem of finding the thermodynamic parameters of point defects – the energy of their formation, the po-

sitions of impurity levels in the energy band structure of a crystal, the energy of defect free vibrations caused by the change of the atomic vibration frequency in a vicinity of the point defect – is brought to the forefront. The concentration of point defects can often be evaluated only knowing the energy of point defect formation, because the values of other two parameters are smaller, as a rule. For this reason, the determination of the formation energy for those defects is of significant practical importance.

In principle, quantum mechanics allows any energy parameter of a system to be determined. However, exact calculations can be performed only for the simplest molecules. In most cases, the available methods for the calculation of the energy of point defect formation in a crystal can be realized only with the use of computation facilities, because they are mainly based on the solution of the Hartree–Fock–Roothan equations. But the application of the energy values obtained for the formation of point defects does not always make it possible to obtain satisfactory correlations, while determining the defect concentration and interpreting the experimental crystal parameters [4]. Bearing this fact in mind, it would be reasonable in some problems dealing with the calculation of the defect formation energy to use those methods, which have a calculation accuracy that is known in advance to be lower, but to consume less computational resources.

One of the ways to do so is a substantial simplification of the Hartree–Fock–Roothan method, which will allow one to obtain the sought result without

engaging considerable computational resources. In particular, in the extended Hückel method, some of the matrix elements are not calculated. Instead, known empirical quantities and their dependences are used. Significant results were obtained within this method for cyclic organic molecules. In works [5, 6], it was applied to determine the energies of vacancy formation in elementary semiconductors belonging to the sixth group and in  $A^{III}B^V$  compound semiconductors.

Another way to calculate the defect formation energy is the method based on the application of thermochemical [7], thermodynamic [8], or electrophysical [9] data. In particular, using such crystal parameters as the atomization energy, the melting energy, and so forth, it is possible to evaluate energy changes in the system occurring, when an atom is removed from its site, and the lattice relaxes in a site vicinity. In other cases, the energies of vacancy formation are calculated on the basis of those experimentally determined parameters of the system, which are the most sensitive to point defects. In particular, these are the compressibility and the concentration of free charge carriers. Since different parameter sets are used in different calculation methods, a comparison of the results obtained is required. In the case of correlation between the numerical values of defect formation energies obtained by different methods, this analysis will allow to draw a conclusion on their applicability to the determination of a point defect concentration in semiconductors.

In this work, the enthalpies for anion and cation monovacancy formation in semiconductor compounds  $A^{II}B^{VI}$ ,  $A^{III}B^V$ , and  $A^{IV}B^{VI}$  are calculated. Those compounds are basic materials for the fabrication of active and passive elements in modern micro- and nanoelectronics. The optimization of the properties of those substances faces a problem dealing with the efficient control over the defect subsystem. This task could be solved, although not in full, provided that reliable information concerning the energy of point defect formation is available.

## 2. Determination of Vacancy Formation Energies Using the Extended Hückel Method

In some cases, the semiempirical procedure of calculation turns out more promising, because the applied empirical parameters reflect those effects that are

neglected in the nonempirical approach. One of the most useful semiempirical methods is the extended Hückel method. In works [5, 6], it was adapted for calculating the enthalpies of vacancy and antistructural defect formation in binary semiconductors.

According to work [5], the enthalpy of the neutral vacancy formation in semiconductors can be calculated by the formula

$$H_V = 4D - E_Z + E_{\text{deform}}, \quad (1)$$

where  $D$  is the energy of one bond in the crystal,  $E_Z$  the formation energy for new bonds, and  $E_{\text{deform}}$  the lattice deformation energy. In work [5], the last term is supposed to be much less than the others, so that its contribution can be neglected. The values of  $D$  are experimentally determined for the majority of semiconductors, and the energy of new bonds is determined in the framework of the defect-molecule model.

Since electrons in tetrahedral structures are in the  $sp^3$ -hybridization state, the wave functions of the atoms around a defect are  $sp^3$ -hybridized atomic orbitals that are centered at the corresponding atoms ( $\varphi_1, \varphi_2, \varphi_3, \varphi_4$ ) and directed to the central atom. If the latter is removed, and if the electrons of the neighboring atoms remain in the  $sp^3$ -hybridized state, the creation of new bonds reduces the system energy by [5]

$$E_Z = nE - 2E_A - (n - 2)E_T. \quad (2)$$

Here,  $n$  is the number of electrons in the system, and  $E_A$  and  $E_T$  are the energies of defect molecule states:

$$E_A = E \frac{1 + 3kS}{1 + 3S}, \quad E_T = E \frac{1 - kS}{1 - S}. \quad (3)$$

The quantity  $E$  in Eq. (2) is the energy of hybridized orbitals in the atoms that surround the vacancy:

$$E = \frac{E_s + 3E_p}{4}, \quad (4)$$

where  $E_s$  is the energy of the atomic  $s$ -orbital, and  $E_p$  the energy of the atomic  $p$ -orbital. The quantity  $E$  can be calculated, by using the values of  $E_s$  and  $E_p$ , which are given, for example, in works [10–14]. The  $E_s$ -values, as well as  $E_p$ -ones, determined in the framework of various methods can differ from one another. However, taking into account that the approximations of the method are crude, the accuracy of their calculation is of no substantial importance.

The overlap integral  $S$  in Eq. (3) can be determined as follows [5]:

$$S = \frac{1}{4} \left( S(s, s) + \frac{4}{\sqrt{2}} S(s, p_\sigma) + 2S(p_\sigma p_\sigma) + S(p_\pi p_\pi) \right). \tag{5}$$

Here, the first three terms characterize the  $\sigma$ -overlapping, and the others the  $\pi$ -overlapping of the neighboring atomic orbitals, which are indicated in parentheses. They can be calculated with the help of numerical integration, by using the Slater functions, e.g., in the framework of Maple’s mathematical environment or using the Batsanov–Zvyagina tables [14] in the standard coordinate system. The effective charge was evaluated, by following the procedures proposed by Slater.

In the approximation of the extended Hückel method, the off-diagonal matrix elements of the Hamiltonian are found as  $h_{ij} = kS(E_i + E_j)/2$  [5], where  $k$  is a model parameter, which is determined by fitting some parameters of the system to their experimental values. In work [5], this parameter was calculated for elementary semiconductors by fitting the theoretically calculated energy  $D$  of one bond in the crystal to known experimental values. The obtained values equal  $k = 2.41$  for C, 1.88 for Si, 1.75 for Ge, and 1.61 for Sn. According to the results of work [6], the

dependence  $k(n)$  is linear:

$$k_n = 1 + \frac{1}{4}(k_4 - 1)n. \tag{6}$$

The results of calculations carried out for  $A^{II}B^{VI}$  and  $A^{III}B^V$  compounds on a basis of the theory presented above are quoted in Table 1.

Attention is attracted by the fact that the formation enthalpies of anion vacancies is lower than the formation enthalpies of cation ones for all compounds. The authors of work [6] assert that this result is natural and, in particular, it explains a shift of the homogeneity interval for those compounds toward the contents with metal excess. However, in the case of  $A^{II}B^{VI}$  compounds, this statement is not valid. In particular, for cadmium telluride, the larger part of the compound existence interval (for zinc telluride, this is the whole interval) corresponds to the excess of the nonmetal component. Therefore, we may assume that the enthalpies of vacancy formation in chalcogenes, which were calculated, by using this method, are some underestimated. It can be a result of violating some theoretical assumptions. In particular, the assumption that the  $sp^3$ -hybridization survives for chalcogene vacancies may be not obeyed, because three of four nearest neighbors of metal atoms from the first coordination sphere are also metal atoms. The linear approximation in the parameter  $k$  can be another possible source of errors.

### 3. Calculation of Vacancy Formation Energies within the Thermodynamic Method

A useful method for the calculation of the vacancy formation energy  $E_V$  was proposed in work [7]. According to it,

$$E_V = E_0 - E_Z + E_K + \Delta E_1 + \Delta E_2. \tag{7}$$

The value of  $E_0$  can be put equal to the energy of compound atomization  $E_{at}$  [18, 21], or it can be determined as the energy of one bond (see the corresponding values in work [10]) times the bond number [15–17].

The quantity  $E_Z$  is the formation energy of new bonds. It is considered to equal the melting energy of pure elements, whose atoms surround the vacancy and form new bonds [7]. Hence, the energy  $E_Z$  is determined by the formula

$$E_Z = \frac{x}{a} \delta_1, \tag{8}$$

*Table 1. Energies of metal,  $V_A$ , and chalcogene,  $V_B$ , vacancy formation in  $A^{III}B^V$  and  $A^{II}B^{VI}$  compounds*

Compound	$E_{V_A}$ , eV	$E_{Z,V_A}$ , eV	$E_{V_B}$ , eV	$E_{Z,V_B}$ , eV
III–V				
GaP	5.73	1.39	5.23	1.89
GaAs	5.29	1.23	4.59	1.93
GaSb	5.07	0.84	4.11	1.81
InP	5.89	1.07	5.70	1.26
InAs	5.14	1.06	4.85	1.35
InSb	4.72	0.88	4.15	1.45
II–VI				
ZnS	5.65	0.71	4.33	2.03
ZnSe	4.48		3.23	
ZnTe	4.08	0.47	2.81	1.71
CdS	5.22	0.45	4.00	1.68
CdTe	3.65	0.47	2.60	1.52

where  $x$  is the number of new bonds (A–A for  $V_B$  or B–B for  $V_A$ ); the parameter  $a = 4$  for  $A^{II}B^{VI}$  and  $A^{III}B^V$  compounds, and 6 for  $A^{IV}B^{VI}$  ones; and  $\delta_1$  is the energy per one bond, which is taken to equal the melting energy of pure elements (A or B, respectively).

The quantity  $E_K$  in Eq. (7) corresponds to the energy of Coulomb interaction between the atoms around the vacancy and equals

$$E_K = \frac{1}{4\pi\epsilon_0} \frac{z_{A,B}^* z_{A,B}^*}{\epsilon r}. \quad (9)$$

Here,  $z^*$  are the effective atomic charges,  $\epsilon_0$  the electric constant,  $\epsilon$  the static dielectric permittivity [3], and  $r$  the distance between the atoms of the same kind. The crystallographic parameters and the static dielectric permittivity for  $A^{II}B^{VI}$  and  $A^{III}B^V$  compounds were taken from works [10] and [3], respectively, and for  $A^{IV}B^{VI}$  compounds from works [21, 25, 26] and [25–29], respectively. According to work [7], when a vacancy is formed, the excess charge emerging as a result of the cation or anion removal becomes uniformly distributed among the atoms of the first coordination sphere. Therefore, the quantity  $z^*$  in formula (9) should be multiplied by factors that take into account both the type of atoms forming the compound and their number in the first coordination sphere. Namely,  $z_A^* = \frac{6}{4}z^*$  and  $z_B^* = \frac{2}{4}z^*$  for  $A^{II}B^{VI}$  compounds;  $z_A^* = \frac{5}{4}z^*$  and  $z_B^* = \frac{3}{4}z^*$  for  $A^{III}B^V$  compounds, and  $z_A^* = \frac{6}{6}z^*$  and  $z_B^* = \frac{4}{6}z^*$  for  $A^{IV}B^{VI}$  compounds.

The fourth and fifth terms in Eq. (7) describe the changes of the binding energy between atoms in the first coordination sphere around a vacancy,  $\Delta E_1$ , and between atoms in the first and the second coordination sphere,  $\Delta E_2$ . However, as was shown in works [16–18], the corresponding contributions to Eq. (7) are insignificant, so that those terms can be neglected.

It is evident that the main origin of calculation errors is the procedure used to determine the quantity  $E_0$ , because the contribution of this term is the largest. At the same time, the spread of corresponding literature data available for some crystals is rather large. For instance, using the value of atomization energy  $E_{at}$  for GaAs from work [18], we obtain  $E_0 = 5.6$  eV. At the same time, the application of the data from work [10] gives rise to  $E_0 = 6.52$  eV. It is worth noting that, in work [7], the value of  $E_0$  was determined as a difference between the sublimation en-

thalpy and the enthalpy of the compound formation from elements under standard conditions. However, the energies of vacancy formation obtained in this case turned out considerably lower than the modern experimental values and the theoretical values calculated by other methods.

The energy of new bond formation,  $E_z$ , is determined on the basis of the data for the melting energy of pure components. The corresponding results are presented in handbooks with a rather high accuracy. The  $S$ -values for  $A^{II}B^{VI}$  and  $A^{III}B^V$  compounds were taken from work [22] and, for  $A^{IV}B^{VI}$  ones, from works [19, 21, 22, 25, 26]. The calculation error for  $E_z$  may be, most probably, a result of the assumption that equality (8) is obeyed. We may suppose that the error for the energy of new bonds will be larger for metalloid vacancies, because the nearest atoms around those defects are metals, which, in their pure form, are characterized by metallic nonlocalized and nondirected bonds.

While calculating the Coulomb energy, we face a problem of correct choice for the effective atomic charge, because the available literature data are considerably different (see Table 2). This is a result of both the difficulty of its experimental determination and the ambiguity of the very notion of the effective atomic charge in crystals with a nonionic character of the bonds [10]. The effective charges can be determined from the data on the degree of bond ionicity in the crystal [19]:

$$z^* = n\sqrt{f_i/k_n}, \quad (10)$$

where  $n$  is the refractive index (for  $A^{II}B^{VI}$  and  $A^{III}B^V$  compounds, its values were taken from work [23], and for  $A^{IV}B^{VI}$  ones from works [23, 29, 30]),  $f_i$  the ionicity, and  $k_n$  the coordination number. Table 2 contains the values for  $f_i$  that were calculated in work [20] on the basis of the data on the elastic coefficient, as well as theoretically calculated in work [10] with the use of hybridized orbitals and only  $p$ -orbitals. One can see that the application of hybridized orbitals makes it possible to obtain values that are almost completely agree with the data of work [20]. On the basis of the presented  $f_i$ -values, the effective charges of atoms in semiconductor compounds were determined (the parenthesized values in Table 2).

Table 2 also presents the ionicities, which were calculated as a function of the difference  $\Delta X$  between

the anion and cation electronegativities [19]:

$$f_i = 1 - e^{-0.18\Delta X^2 \frac{\nu}{N}}. \quad (11)$$

Here,  $\nu$  is the valence, and  $N$  the coordination number. The obtained  $f_i$ -values are somewhat different from those presented in works [10, 20]. However, the  $z^*$ -values determined with their help are very close to those used most often in the literature. This circumstance is especially evident for GaAs and GaSb, for

**Table 2. Bond ionicities and effective atomic charges in semiconductor crystals**

Compound	$f_i(z^*, e)$	$z^*, e$
GaAs	0.32 [20](0.48 <sup>1</sup> ) 0.32 <sup>h</sup> ; 0.47 <sup>p</sup> [10] (0.48 <sup>1</sup> ) 0.26 [19] (0.43 <sup>1</sup> )	0.51; 0.46 [18] 0.17(ssd) 0.17(xrd) [19]
GaSb	0.27 [20](0.51 <sup>1</sup> ) 0.27 <sup>h</sup> ; 0.45 <sup>p</sup> [10] (0.51 <sup>1</sup> ) 0.16 [19] (0.39 <sup>1</sup> )	0.33 [18] 0.13(ssd) [19]
ZnS	0.63 [20](0.48 <sup>1</sup> ) 0.56 <sup>h</sup> ; 0.75 <sup>p</sup> [10](0.45 <sup>1</sup> )	0.85 [18] 0.44(ssd) [19]
ZnTe	0.55 [20](0.66 <sup>1</sup> ) 0.54 <sup>h</sup> ; 0.74 <sup>p</sup> [10](0.65 <sup>1</sup> ) 0.305 [19](0.49 <sup>1</sup> ) 0.39 [19*](0.56 <sup>1</sup> )	0.39(ssd)[19]
CdS	0.69 [20](0.52 <sup>1</sup> ) 0.63 <sup>h</sup> ; 0.80 <sup>p</sup> [10](0.50 <sup>1</sup> ) 0.45 [19*](0.42 <sup>1</sup> )	0.45–0.90 [18] 0.34(ssd); 0.17(xrd)[19]
CdTe	0.68 [20](0.57 <sup>1</sup> ) 0.60 <sup>h</sup> ; 0.78 <sup>p</sup> [10](0.53 <sup>1</sup> ) 0.32 [19](0.39 <sup>1</sup> ) 0.40 [19*](0.44 <sup>1</sup> )	0.62–0.95 [18] 0.38(ssd); 0.22(xrd) [19]
GeS	0.29 [19]	0.20(ssd) [19]
GeSe	0.26 [19](0.21 <sup>1</sup> )	0.17(ssd) [19]
GeTe	0.16 [19](0.41 <sup>1</sup> )	
PbS	0.39 [19](0.385 <sup>1</sup> )	0.35(ssd) [19]
PbTe	0.23 [19](0.30 <sup>1</sup> )	0.28(ssd) [19]
SnTe	0.23 [19]	0.26(ssd) [19]

<sup>1</sup> calculation by Eq. (10) according to work [14], <sup>h</sup> calculated with the use of hybridized orbitals, <sup>p</sup> calculated with the use of *p*-orbitals, (ssd) spectroscopic data, (xrd) X-ray spectroscopic data, \*  $f_i$  calculated with the use of the tellurium electronegativity  $X = 2.34$  [19].

which the values 0.46 and 0.33, respectively, are used most often.

Attention should be paid to underestimated values of  $z^*$  for zinc and cadmium tellurides. They were calculated on the basis of the ionicity data taken from work [19], in which, as was already mentioned above, the value of  $f_i$  was determined in terms of the electronegativity difference. There are several electronegativity systems. Therefore, it is possible to choose a system, in which the electronegativity difference and, accordingly, the effective charges for ZnTe and CdTe are maximum. In particular, in the geometrical electronegativity system [19],  $X = 1.05$  for Cd, which is different from the value  $X = 1.2$  given in Table 3. At the same time, for tellurium,  $X = 1.1$  in two systems. A similar result can be obtained, if the electronegativities are calculated on the basis of the data on the ionization energy and the electron affinity [19]. In this case,  $X = 2.34$  for tellurium. However, it is difficult to determine the electronegativities of cadmium and zinc in this system because of a considerable influence of *d*-electrons. If we put those parameters to equal the values presented in Table 3, the obtained  $z^*$ -value correlates much better with other tabulated data.

The results of calculations performed in the framework of the method described above are shown in Table 3. Two values for the formation energy  $E$  correspond to the minimum,  $E_{\min}$ , and maximum,  $E_{\max}$ , values of  $E$ . The former was determined, by using the atomization energy values that were applied, while finding  $E_0$  with regard for the smallest  $z^*$ -value obtained from formula (10). The latter,  $E_{\max}$ , was calculated, by using the magnitudes of binding energy from work [10] and the largest of the  $z^*$ -values obtained from formula (10).

In addition to the literature data [19], the atomization energies for germanium chalcogenides were also calculated, by summing up the formation enthalpies for their compound components [24]:

$$E_{\text{at}} = \Delta H_f^0(A) + \Delta H_f^0(B) + \Delta H_f^0(AB).$$

When determining the effective charges in the case of germanium sulfide, the refractive index was considered to be equal to the corresponding value for germanium selenide. Since the crystals of  $A^{\text{IV}}B^{\text{VI}}$  compounds are characterized by high values of dielectric permittivity (see Table 3), the contribution of the

Table 3. Crystal parameters of  $A^{III}B^V$ ,  $A^{II}B^{VI}$ , and  $A^{IV}B^{VI}$  compounds and the corresponding energies of vacancy formation

Parameter	GaAs	GaSb	ZnS	ZnTe	CdS	CdTe	GeS	GeSe	GeTe	SnTe	PbS	PbTe
4D, eV [10]	6.52	5.92	6.36	4.56	6.68	4.12						
$E_{at}$ , eV	5.6 [18] 6.36 [21]	5.24 [18] 5.96 [21]	4.88 [18]	3.88 [18]	4.2 [18]	3.52 [18]	7.42 [19] 7.70 *	6.61 *	6.12 [19] 6.11 *	5.76 [25]	5.82 [25]	4.56 [26]
$X_A$ [19]	1.5	1.5	1.25	1.25	1.2	1.2	1.7	1.7	1.7	1.5	1.5	1.5
$X_C$ [19]	2.2	1.9	2.5	2.1	2.5	2.1	2.5	2.4	2.1	2.1	2.5	2.1
$z^*$ , $e_0$	0.43	0.39	0.395	0.56	0.42	0.44	0.20	0.17	0.41	0.26	0.35	0.28
$E_{V_A}, E_{V_B}$ , eV ( $E_{min}$ )	5,21; 6.01	5,03; 5.47	4,96; 5.71	3,77; 5.16	4,28; 5.00	3,34; 4.21	7,69; 7.01	6,50; 5.92	5,85; 5.58	5,40; 5.62	5,80; 5.41	4,20; 4.13
$z^*$ , $e_0$	0.48	0.51	0.48	0.66	0.52	0,57						
$E_{V_A}, E_{V_B}$ , eV ( $E_{max}$ )	6,17; 7.05	5,80; 6.37	6,49; 7.65	4,51; 6.38	5,81; 6.95	3,99; 5.33						

\* calculated according to the data of work [19]

Coulomb term to the total energy of vacancy formation is insignificant, and such a substitution will not affect the result of calculations substantially. For instance, the values of  $E_K$  calculated by formula (9) for germanium chalcogenides fall within an interval of 0.02–0.03 eV; for lead chalcogenides, for which  $\varepsilon$  is an order of magnitude larger, this term can be neglected altogether. Hence, the choice of effective charges for atoms in  $A^{IV}B^{VI}$  compounds is not so important as for  $A^{III}B^V$  and  $A^{II}B^{VI}$  crystals.

#### 4. Calculation of Schottky Defect Formation Energies with the Use of Mie–Lennard-Jones Pair Interaction Potentials

In works [8, 31], a method for the determination of formation enthalpies for Schottky defects,  $h_S$ , with the use of pair interaction potentials was proposed. According to work [8],

$$h_S = E_S + \frac{\alpha_p T D a b}{3(b-a)} (K_S X^b - X^a), \quad (12)$$

where

$$E_S = \frac{D}{b-a} (a K_S X^b - b X^a), \quad (13)$$

$$K_S = 1 + \frac{5b(b+1)}{16}, \quad (14)$$

$$X = \left(1 + \frac{\alpha_p T}{3}\right)^{-1}, \quad (15)$$

and  $\alpha_p$  is the thermal expansion coefficient. The quantities  $D$ ,  $a$ , and  $b$  are the parameters of the Mie–Lennard-Jones pair interaction potential, which describes the interaction between the nearest neighbors:

$$W(r) = \frac{D}{b-a} \left[ a \left( \frac{r_0}{r} \right)^b - b \left( \frac{r_0}{r} \right)^a \right], \quad (16)$$

where  $r_0$  is the potential minimum coordinate. For crystals,  $r_0$  can be put equal to the shortest distance between different atoms.

The parameter  $b$  was determined according to the formula [32]

$$b = 6\gamma_0 \left[ 1 - \left\{ \frac{8D}{k\theta_0} - 2 \right\}^{-1} \right] - 2 \approx 6\gamma_0 - 2, \quad (17)$$

where  $\gamma_0$  is the Grüneisen parameter, and  $\theta_0$  the Debye temperature at  $T = 0$  K. In order to find the parameter  $a$ , three formulas with different sets of experimental parameters were used [32, 33]:

$$a = b \frac{\Gamma}{K_R + \Gamma}, \quad (18)$$

$$\text{where } K_R = \frac{h^2}{4k\pi^2 r_0^2 M}, \Gamma = \frac{144}{5k_n} \frac{\theta_0}{b(b+1)} \frac{k\theta_0}{8D}, \quad (19)$$

$M$  is the atomic mass, and  $k_n$  the coordination number;

$$a = B \frac{3\pi r_0^3}{k_n k_y b D}, \quad (20)$$

Table 4. Crystal parameters of  $A^{II}B^{VI}$ ,  $A^{III}B^V$ , and  $A^{IV}B^{VI}$  compounds, and parameters of enthalpies of Schottky defect formation

Parameter	ZnS	ZnTe	CdS	CdTe	GaAs	GaSb	PbS	PbTe
$\mu$ , (300 K)	0.38 [51] 0.37 <sup>1</sup> [36] 0.38 <sup>1</sup> (0.38 <sup>1</sup> ) <sup>a</sup> [50]	0.36 [51] 0.36 <sup>1</sup> [36]	0.40 [51] 0.39 <sup>1</sup> [36]	0.41 [23] 0.39 <sup>1</sup> [36] 0.39 <sup>1</sup> (0.39 <sup>1</sup> ) <sup>a</sup> [51]	0.31 [51] 0.31 <sup>1</sup> [36]	0.31 [51] 0.32 <sup>1</sup> [36]	0.19 [51] 0.13 <sup>1</sup> [10] 0.39 <sup>2</sup> [10]	0.67 [51] 0.36 <sup>2</sup> [10]
B, GPa (300 K)	83.04 [37]	56.02 [37]		46.52 [37]			62.8 [51] 54.6 [51] <sup>a</sup>	39.8 [51] 39.6 [51] <sup>a</sup>
	71.9 <sup>3</sup> [36] 100.4 <sup>4</sup> [36]	50.8 <sup>3</sup> [36] 65.9 <sup>4</sup> [36]	58.4 <sup>3</sup> [36] 78.0 <sup>4</sup> [36]	42.4 <sup>3</sup> [36] 56.9 <sup>4</sup> [36]	77.0 <sup>3</sup> [36] 99.9 <sup>4</sup> [36]	56.3 <sup>3</sup> [36] 71.3 <sup>4</sup> [36]	62.2 <sup>3</sup> [10] 49.0 <sup>4</sup> [10]	40.8 <sup>3</sup> [10] 82.2 <sup>4</sup> [10]
$\theta$ , K (300 K)	334 ± 6 [50] <sup>a</sup> 315 <sup>c</sup> [49]	250 <sup>c</sup> [49] 300 [53]	250 [53] <sup>a</sup>	161 ± 4 [50] <sup>a</sup> 200 <sup>c</sup> [49] 355 [56] 362 [20]	275 [55] <sup>a</sup> 250 [56]		149 [57] <sup>b</sup> 227 [25] <sup>d</sup>	127 [57] <sup>b</sup> 125 [25] <sup>d</sup>
	441 <sup>6</sup> [47] 206 <sup>5</sup> [47] 282.2 <sup>7</sup> [36] 324.1 <sup>8</sup> [36]	252.5 <sup>6</sup> [52]	352.2 <sup>6</sup> [54]	206 <sup>6</sup> [47] 100 <sup>5</sup> [47] 134.5 <sup>7</sup> [36] 150.0 <sup>8</sup> [36]	290.3 <sup>7</sup> [36] 334.0 <sup>8</sup> [36]	222.9 <sup>7</sup> [36] 254.3 <sup>8</sup> [36]	313.0 <sup>7</sup> [10] 254.3 <sup>8</sup> [10]	464.6 <sup>7</sup> [10] 208.6 <sup>8</sup> [10]
$\gamma$ (300 K)	0.21 ( $\gamma_{TA}$ ) [58] 1.33 ( $\gamma_{LA}$ ) [58] 2.33 <sup>9</sup> [36] 2.41 <sup>10</sup> [55]	2.19 <sup>9</sup> [36] 2.22 <sup>10</sup> [55]	2.53 <sup>9</sup> [36] 2.63 <sup>10</sup> [52]	2.54 <sup>9</sup> [36] 2.74 <sup>10</sup> [51]	1.87 <sup>9</sup> [36] 1.83 <sup>10</sup> [51]	1.89 <sup>9</sup> [36] 1.83 <sup>10</sup> [51]	2.52 [37] 2.50 [37] 1.04 <sup>9</sup> [10] 1.24 <sup>10</sup> [51]	1.96 [37] 2.18 [37] 0.27 <sup>9</sup> [10] 1.94 <sup>11</sup> [47]
$h_S + D$ , eV (300 K) Eq. (18) $a(\theta)$	8.49 (0 K) 8.08 (80 K) 11.25 <sup>12</sup>	8.67 (80 K)	7.86 (0 K) 9.45 11.4 <sup>12</sup>	6.16 (0 K) 7.82 (80 K) 8.11 <sup>12</sup>	8.99 (0 K) 11.72	9.69	6.15 (20 K) 7.87 (200 K)	5.36 (20 K)
$h_S + D$ , eV (300 K) Eq. (20) $a(B)$	8.86 9.77	7.54 8.34		7.09 7.65			5.93 (0 K) 6.10 (200 K)	4.86 (0 K) 4.86 (200 K)
$h_S + D$ , eV (300 K) Eq. (21) $a(\mu)$	9.84 (0 K) 9.7	8.27	9.03	7.86 (0 K) 7.66	11.03	9.98	6.16 (200 K)	

<sup>a</sup> coefficient values at  $T = 0$  K, <sup>b</sup> coefficient values at  $T = 20$  K, <sup>c</sup> coefficient values at  $T = 80$  K, <sup>d</sup> coefficient values at  $T = 200$  K, <sup>1</sup> calculated by Eq. (32), <sup>2</sup> calculated by Eq. (33), <sup>3</sup> calculated by Eq. (29), <sup>4</sup> calculated by Eq. (30), <sup>5</sup> calculated by Eq. (26) according to the data for  $\theta_{TO}$  and  $\theta_{LO}$  from works [47, 52, 54], <sup>6</sup> calculated by Eq. (27) according to the data for  $\theta_{TO}$  and  $\theta_{LO}$  from work [51], <sup>7</sup> calculated by Eq. (28), Poisson's ratio by Eq. (32), and compression modulus by Eq. (29), <sup>8</sup> calculated by Eq. (28), Poisson's ratio by Eq. (32), and compression modulus by Eq. (30). <sup>9</sup> calculated by Eq. (22), <sup>10</sup> calculated by Eq. (23), <sup>11</sup> calculated by Eq. (25), <sup>12</sup> calculated using  $\theta$  determined on the basis of  $\theta_{LO}$  and  $\theta_{TO}$ .

where  $B$  is the compression modulus, and  $k_y$  the packing coefficient; and

$$a = -\frac{(\mu + 1) 6MV_L^2}{(\mu - 1) bk_n D}, \quad (21)$$

where  $\mu$  is Poisson's ratio, and  $V_L$  the longitudinal sound velocity.

The results of calculations for the enthalpies of Schottky defect formation at  $T = 0$  and 300 K are shown in Table 4. The crystallographic parameters of the substances were taken from works [10, 25, 26, 46], the densities from work [47], the atomic masses from work [22], and the thermal expansion coefficients from works [23, 25, 48, 49]. In order to calculate the total energy of formation of two isolated cation and anion

vacancies,  $h_S$  should be summed up with  $D$  [34]. The  $h_S$ -values, which were obtained by using various formulas for the determination of the parameter  $a$ , agree well with each other. In particular, the enthalpies of Schottky defect formation that were calculated by formulas (20) and (21) are close to each other, but they are some different from the values obtained with the use of formula (18).

As one can see from Table 4, the energy of Schottky defect formation is the smallest in lead telluride and lead sulfide, and the largest in gallium arsenide and gallium antimonide. From whence, it follows that the formation of Schottky defects is the most energetically beneficial in  $A^{IV}B^{VI}$  compounds. This effect is much less pronounced in  $A^{II}B^{VI}$  and, especially,  $A^{III}B^V$  compounds. The  $h_S$ -values quoted in Table 4 for  $A^{II}B^{VI}$  and  $A^{III}B^V$  semiconductors were obtained, by using the binding energy values taken from work [10]. If, instead of those values, the atomization energies from work [18] are used, the enthalpy of defect formation decreases a little. For instance, the application of the value  $D = 0.88$  eV [18] instead of  $D = 1.03$  eV [10] for cadmium telluride results in the growth of the defect formation enthalpy from 3.63 to 3.84 eV, i.e. by about 5%.

The Grüneisen parameter  $\gamma$  was calculated using the following analytic dependences, which allow this quantity to be determined in terms of either the known stiffness coefficients  $C_{ij}$  or Poisson's ratio  $\mu$  [35]. Namely,

$$\gamma = \frac{9(V_L^2 - 4/3V_T^2)}{2(V_L^2 + 2V_T^2)}, \quad (22)$$

$$\gamma = \frac{3}{2} \left( \frac{1 + \mu}{2 - 3\mu} \right). \quad (23)$$

Here,  $V_L$  and  $V_T$  are the longitudinal and transverse components of the sound velocity:

$$V_L = \left[ \frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho} \right]^{1/2}, \quad (24)$$

$$V_T = \left[ \frac{C_{11} - C_{12} + C_{44}}{3\rho} \right]^{1/2},$$

where  $\rho$  is the density. For  $A^{II}B^{VI}$  and  $A^{III}B^V$  compounds, the coefficients  $C_{ij}$  at  $T = 0$  and 300 K were taken from works [36,50] and, for  $A^{IV}B^{VI}$  compounds, from work [10].

As one can see from Table 4, the both formulas give almost identical values for the parameter  $\gamma$ ,

which, nevertheless, are different from the literature data. While determining the Grüneisen parameter  $\gamma$  for lead telluride, which is characterized by the relation  $C_{12} - C_{44} < 0$ , the dependence [36]

$$\gamma = \left[ -(C_{12} - C_{44}) \frac{V_z}{27s} \frac{1}{kT} \right]^{1/2}, \quad (25)$$

where  $V_z$  is the unit cell volume, and  $s$  the number of atoms per unit cell, was applied. As a result of this calculation, the obtained  $\gamma$ -value turned out very close to that presented in work [37] ( $\gamma = 1.96$ ).

As was shown in work [38], the numerical value of Grüneisen parameter falls within the interval  $0.67 < \gamma < 1.21$ . If the  $\gamma$ -value goes beyond these limits, this means that the temperature dependence of the Debye temperature was not taken into consideration at its determination [38]. Nevertheless, despite the values obtained by us for  $\gamma$  go beyond the indicated limits, the calculated enthalpies of defect formation agree with literature data. Using the coefficients  $C_{ij}$  determined at  $T = 0$  and 300 K for the calculation of  $\gamma$ , it is found that the temperature dependence of the Grüneisen parameter is weak, so that it can be ignored in calculations. For example, for zinc sulfide,  $\gamma = 2.33$  at  $T = 0$  K and 2.37 at  $T = 300$  K, which practically does not affect the result of calculations for  $h_S$ .

As was marked in works [38–41], the application of formula (18) for the calculation of the quantities  $a$  and  $h_S$  requires that the temperature dependences of the Debye temperature should be selected carefully, because the indicated parameters considerably affect the result of calculations. For some semiconductors, there are no reliable data concerning the Debye temperature at various  $T$ . Therefore, its values were determined with the use of partial Debye temperatures for acoustic or optical phonons according to the dependence [42]

$$\theta = \left[ \frac{2}{3}\theta_{TA}^2 + \frac{1}{3}\theta_{LA}^2 \right]^{1/2} \quad (26)$$

or [43]

$$\theta = \left[ \frac{3}{1/\theta_L^2 + 2/\theta_T^2} \right]^{1/3}. \quad (27)$$

We also used the following formula proposed in work [44]:

$$\theta = \frac{h}{2\pi k} \left( \frac{6\pi^2\rho}{M} \right)^{1/3} K(\mu) \sqrt{\frac{B}{\rho}},$$

where

$$K(\mu) = \left[ \frac{1}{3} \left[ \left[ \frac{1+\mu}{3(1-\mu)} \right]^{3/2} + 2 \left[ \frac{2(1+\mu)}{3(1-2\mu)} \right]^{3/2} \right] \right]^{-1/3}. \quad (28)$$

The data from Table 4, e.g., for CdS and GaSb, testify that the evaluation of the Debye temperature at 300 K on the basis of partial Debye temperatures for optical phonons gives a little overestimated value for  $\theta$ . Therefore, the energies of Schottky defect formation at  $T = 300$  K calculated by formula (18) will also be overestimated. The application of dependence (27) gives an underestimated value of the Debye temperature for A<sup>IV</sup>B<sup>VI</sup> and GaAs compounds, whereas rather a good coincidence with the experiment was obtained in the GaSb case.

The analysis of the data for the defect formation enthalpy presented in Table 4 testifies that the  $h_S$ -values obtained for ZnTe and CdTe at 300 K agree well with the results of other calculations for this temperature. At the same time, the  $h_S$ -values for ZnS and CdS expectedly turned out overestimated.

It is worth noting that the Debye temperature change by approximately 30 K results in the variation of the vacancy formation enthalpy by about 1 eV. This fact stimulated us to critically analyze the values of the parameter  $a$  and the Schottky defect formation enthalpy obtained using formula (18). If formulas (20) and (21) are used for the determination of  $h_S$ , the choice of the specific value of Debye temperature is not crucial, because  $\theta$  does not enter these formulas explicitly, and the parameter  $b$  is practically independent of it. Therefore, provided that the temperature dependences of the compression modulus  $B$  and the stiffness coefficients  $C_{ij}$  are known, the dependence  $h_S(T)$  can be found, by using formulas (20) and (21) and making no allowance for the temperature dependence of the Debye temperature. The results of corresponding calculations carried out for ZnS, CdTe, PbS, and PbTe demonstrated that the enthalpy of Schottky defect formation changes much less with the temperature than it follows from formula (18).

In addition to experimental measurements of the compression modulus  $B$  in works [37, 51], it was also calculated theoretically: by formula

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (29)$$

in work [10] and by formula

$$B = \rho V_K^2 \frac{1+\mu}{1-3\mu} \quad (30)$$

in work [35]. Here,  $V_K$  is the sound velocity, which is determined by the formula

$$V_K^2 = \frac{V_L^2 + 2V_T^2}{3}, \quad (31)$$

where  $V_L$  and  $V_T$  are its longitudinal and transverse, respectively, components. As one can see from the results of calculations presented in Table 4, formula (28) underestimates and formula (29) overestimates the compression modulus values in comparison with experimental data. The application of the experimentally determined  $B$ -value for the calculation of the parameter  $a$  by formula (9) and the further calculation of the enthalpies of Schottky defect formation bring about  $h_S$ -values that are less than those obtained from formulas (18) and (20). A better correlation is achieved if the compression moduli are determined from formula (29). It should be noted that the same effect – a better correlation with experimental data, when the  $B$ -values determined by formula (29) are used – takes place as well, when the Debye temperatures are calculated by formula (27). In this case, for some crystals, the given values exceed the experimentally determined ones by more than 20%.

The calculation of Poisson's ratio with the help of the formula [35]

$$\mu = \frac{1}{2} \frac{(V_L/V_T)^2 - 2}{(V_L/V_T)^2 - 1} \quad (32)$$

gave rise to numerical values that almost completely coincided with literature data, which testifies to the reliability of the obtained  $\mu$ -values and the coefficients  $C_{ij}$  that were used in the calculation. A<sup>IV</sup>B<sup>VI</sup> compounds comprised an exception, because formula (29) did not give satisfactory  $\mu$ -values for them. Therefore, for those crystals, we used the following formula [35], by assuming the Grüneisen parameter  $\gamma$  to be known [37]:

$$\mu = \frac{1}{3} \frac{4\gamma - 3}{2\gamma + 1}. \quad (33)$$

Using the obtained  $\mu$ -values and formula (21), the enthalpies of defect formation at 300 K (for ZnS and

CdTe also at 0 K) are calculated. As a result, it is found that, contrary to the dependence obtained with the use of formula (18),  $h_S$  for ZnS and CdTe decreases, as the temperature grows.

While calculating the temperature dependence  $h_S(T)$  with the help of formula (21), one should bear in mind that the calculation of Poisson's ratio  $\mu$  at  $T = 0$  K is carried out on the basis of data on  $C_{ij}$ . In so doing, the stiffness coefficients are not measured at this temperature; instead, they are calculated by extrapolating the experimental dependence  $C_{ij}(T)$  registered at nitrogen temperatures. Therefore, there is a possibility to obtain a rather high error in the relevant calculations. Hence, it is expedient to use formula (18) for the determination of  $h_S$  at low temperatures (in a vicinity of 0 K) and formulas (20) and (21) at high ones.

It is also worth noting that the theory used in this work to calculate the enthalpies of Schottky defect formation was developed in work [8] for ionic crystals. The major defects in the latter are vacancies in the anion and cation sublattices [45], which are responsible for the temperature dependences of key parameters of the crystal ( $\alpha_p$ ,  $C_{ij}$ , and  $B$ ). In covalent crystals, the parameters used for the determination of  $h_S$  can be affected, besides vacancies, also by interstitial atoms and various complexes, the concentrations of which are high, especially at high temperatures [3]. Therefore, the results for  $h_S$  at 0 K may have a considerable error in the case of crystals, in which Schottky defects do not dominate.

### 5. Calculation of Vacancy Formation Energies on the Basis of Hall Measurements

The energy of point defect formation,  $E$ , can be determined by interpreting the results of measurements of the Hall charge carrier concentration  $n_x$  in the framework of the defect subsystem model, in which  $E$  is the variational parameter. From this point of view, the most practical procedure includes the measurements of  $n_x$  under the conditions of two-temperature crystal annealing and the construction of the dependences of the Hall concentration on the annealing temperature at a fixed pressure of vapor component,  $n_x(T)$  and on the vapor pressure at a fixed annealing temperature,  $n_x(T)$ . Under those conditions, the equilibrium concentrations of vacancies ( $V_A$  and  $V_B$ ), interstitial atoms ( $A_i$  and  $B_i$ ), and antistructural atoms ( $A_B$  and  $B_A$ ) in a crystal of a binary compound can be deter-

mined from the condition of thermodynamic equilibrium at the given pressure  $P$  and temperature  $T$  in a heterogeneous system [59]:

$$-\mu_{V_A}^s = \mu_A^g; \quad \mu_{A_i}^s = \mu_A^g; \quad \mu_{V_B}^s + \mu_A^g = \mu_{A_B}^s, \quad (34)$$

$$-\mu_{V_B}^s = \mu_B^g; \quad \mu_{B_i}^s = \mu_B^g; \quad \mu_{V_A}^s + \mu_B^g = \mu_{B_A}^s. \quad (35)$$

Here,  $\mu_{A,B}^g$  are the chemical potentials of the vapor of a metal ( $A$ ) or nonmetal ( $B$ ), and  $\mu_{[D]}^s$  the chemical potential of defects ( $D$ ) in the crystal. The chemical potential of vapor equals [60]

$$\mu^g = kT \ln P + \mu_0. \quad (36)$$

The determination procedure for the chemical potentials of defects includes the differentiation of the Gibbs energy of a crystal,  $G$ , with respect to the defect concentration. The Gibbs energy can be expressed in the form [9, 61–64]

$$G = G_0 + \sum (E + F_{\text{vib}}) [D] + nE_C - pE_V - T(S_n + S_p + S_k). \quad (37)$$

Here,  $G_0$  is the Gibbs energy component that does not depend on the presence of defects;  $E$  the energy of defect formation;  $F_{\text{vib}}$  the energy of free defect vibrations;  $[D]$  the concentration of defects of the type  $D$ ;  $n$  and  $p$  are the concentrations of electrons and holes, respectively;  $E_C$  and  $E_V$  are the energies of the conduction band bottom and the valence band top, respectively;  $S_k$  is the configurational entropy; and  $S_n$  and  $S_p$  are the entropies of electrons in the conduction band and of holes in the valence band, respectively. The summation is carried out over all sublattices and all defects in the sublattice. The energy of free crystal vibrations changes by

$$F_{\text{vib}} = \pm \{3kT \ln (T_\theta/T) - kT\} + x \cdot 3kT \ln (\omega/\omega_0), \quad (38)$$

when a defect is formed. Here,  $x$  is the number of atoms that changed the frequency  $\omega_0$  of their vibrations in a perfect crystal to the frequency  $\omega$  of their vibrations in a vicinity of the defect. The parameter  $x$  is assumed to be equal to the number of atoms in the first coordination sphere around the defect. The entropy can be determined, by using the Boltzmann law

$$S_k = k \ln(W), \quad (39)$$

where  $W$  is the thermodynamic probability. The configurational entropy of a crystal with  $j$  sublattices

(anions, cations, interstitial voids), with defects of several different types in each of them, equals

$$S_k = k \ln \left( \prod_j W_j \right), \quad (40)$$

$$W_j = \frac{N_J!}{(N_J - \sum [D])! \prod [D]!},$$

where  $N_J$  is the concentration of those sites, at which a defect can be formed. For electrons and holes, the thermodynamic probabilities equal

$$W_n = \frac{N_C!}{(N_c - n)!n!}, \quad W_p = \frac{N_V!}{(N_V - p)!p!}. \quad (41)$$

Here,  $N_C$  and  $N_V$  are the densities of states in the conduction and valence bands, respectively; and  $E_g$  is the energy gap width.

Hence, in order to determine the equilibrium concentration of defects at the given values of the annealing temperature and the component vapor pressure, a system of equations of type (34)–(35) has to be solved. The energy of neutral defect formation and the variation of the atomic vibration fre-

quency in vicinities of defects are the model parameters, which are fitted to achieve the best agreement between the theoretical and experimental dependences  $n_x(T, P)$ . Concerning  $A^{II}B^{VI}$  and  $A^{IV}B^{VI}$  compounds, the most reliable information on the dependence of the free charge concentration in them on the technological parameters of a two-temperature annealing is available for zinc [62,63], cadmium [9,61], and lead [64] tellurides.

The defect concentrations were determined, by numerically solving the system of equations (34), (35). Namely, the quadratic function of the residual magnitudes,  $L_{\min} = \sum |\pm\mu_i^s - \mu_i^g|^2$  was minimized. By varying the quantities  $E$  and  $\omega/\omega_0$ , a satisfactory agreement between the theoretical and experimental dependences  $n_x(T, P)$  is obtained in rather wide intervals of annealing temperatures and component vapor pressures. This result testifies to the adequacy of the model proposed for the defect subsystem and the correctness of the values obtained for the energies of defect formation (see Table 5).

## 6. Antistructural and Interstitial Atoms

In comparison with the calculation of vacancy formation energies, the calculation of the formation energies for antistructural and interstitial atoms is a more complicated task, because the corresponding modifications occurring in the electron subsystem are substantial. Therefore, only *ab initio* methods are used, as a rule, while solving such problems. However, by retaining only the first two terms in formula (7), the latter can be used to estimate the formation energies for antistructural defects.

In view of different numbers of bonds in the compound and in the crystals of corresponding components, the relevant formula looks like

$$E_{A_B(B_A)} = E_0 - x_1 \frac{E_{\text{at},A(B)}}{x_2}. \quad (42)$$

Here, the parameter  $E_0$  is put equal to the energy of compound atomization, as was done in formula (7);  $x_1$  is the number of bonds between the nearest neighbors in the AB compound,  $E_{\text{at},A(B)}$  are the atomization energies for pure components, and  $x_2$  is the number of bonds between the nearest neighbors in the structures composed of pure components. The energy values calculated in this way are shown in Table 6. One can see that the formation energies of an-

Table 5. Energies of vacancy formation,  $E$ (eV), in binary semiconductors determined from Hall measurements [9, 61–64]

	ZnTe	CdTe	PbTe
$E_{V_A}$	4.59	3.6 (3.66( $V_{\text{Cd}}^{1-}$ ))	4.18
$E_{V_B}$		3.24(3.75 ( $V_{\text{Te}}^{2+}$ ))	3.19

Table 6. Energies (in electronvolts) of antistructural defect formation in crystals

Compound	$H_{A_B}$	$H_{B_A}$
GaAs	5.58 2.85* [67]	5.49 2.27* [67]
GaSb	4.98	5.06
ZnTe	3.77	4.21
CdTe	3.43 3.92* [69]	3.77 3.70* [69] 3.3** [4]
PbTe	2.72	4.03
GeTe	4.2	5.58

\* theory, \*\* experiment.

tistructural defects increase in the direction from germanium telluride to germanium sulfide. This result is quite natural. It is connected with a reduction of the atomization energies of pure components along this series. The neglect of the fourth and fifth terms in Eq. (7), when Eq. (42) was derived, is more or less justified, because deformations in vicinities of antistructural defects are small. At the same time, the Coulomb term should enter the energy of a new bond created between the atoms of the same kind, which is considered to equal the atomization energy of pure components. However, for  $A^{IV}B^{VI}$  compounds, taking their high dielectric permittivities into account, the neglect of the Coulomb term, similarly to what was done in the calculation of the vacancy formation energies, should not insert a considerable error into the results of calculations. In the case of  $A^{II}B^{VI}$  and  $A^{III}B^V$  compounds, taking into consideration that their dielectric permittivities are much lower than those for the chalcogenides of the fourth-group metals, the assumption about an insignificant contribution of the Coulomb term is not well substantiated. However, our calculation – in particular, for CdTe – brought about a value that agrees well with the literature data. The closeness of the values obtained can be regarded as quite satisfactory.

It is also worth noting that the energies of antistructural defect formation determined in this way were successfully used in works [65, 66], while simulating the defect subsystems of GeTe and SmS crystals. On the other hand, the values obtained for GaAs turned out much larger, than those reported in work [67]. However, reliable works can be found only for cadmium telluride. In those works, the existence of a significant amount of antistructural defects was proved [4, 68], which allows the results of theoretical calculations for the energies of antistructural defect formation to be compared with the values obtained in the simulation. For other compounds, additional researches are required.

An even more complicated situation takes place, while determining the formation energies for interstitial atoms. The formation of the latter stimulates considerably larger lattice deformations in comparison with those arising in the cases of vacancies and antistructural defects, and, respectively, results in a stronger electron redistribution, which makes the application of *ab initio* methods obligatory. In addition, even the application of first-principle methods, but

together with unsatisfactorily chosen model parameters, may give rise to doubtful results. For example, the energies of interstitial atom formation in GaAs (about 5 eV), which were obtained in work [67], seem to be too high. In work [3], the energy of interstitial atom formation was proposed to be evaluated according to the formula

$$E = zE_g/2, \quad (43)$$

where  $z$  is approximately equal to the valency. This expression gives 1.6 eV for the energy of interstitial atom formation in cadmium telluride at  $T = 0$  K, whereas the *ab initio* calculated values amount to 0.76 and 1.09 eV [70] or to 2.04 and 2.26 eV [69] (the first values correspond to the anion and the second ones to the cation environment of the interstitial atom).

In the simulation of the defect subsystem, the optimal values determined by different authors also fall within the indicated intervals [4, 68, 71]. In the case of the interstitial tellurium atom, the *ab initio* calculated values amount to 0.48 and 0.85 eV [70] or to 3.52 and 3.41 eV [69]. The most optimum values determined in works [68, 72] amount to 1.93 [68] and 1.45 eV [72], which are also very close to a value of 1.6 eV. Hence, dependence (43) proposed in work [3] can be used for approximate estimation.

## 7. Discussion of the Results Obtained and Conclusions

In Table 7, the formation energies determined by various methods for anion and cation vacancies are quoted. With regard for the approximate character of the methods used in calculations, the correlation between the obtained results can be regarded as satisfactory. The majority of the numerical values for the vacancy formation energies agree with one another and with the literature data to within about 20%.

Notwithstanding the already marked specific features of the results calculated by each of the methods, some more regularities should be mentioned. In particular, for  $A^{II}B^{VI}$  compounds, the formation energies calculated for anion vacancies within the extended Hückel method are almost the average values for the values obtained by the method, in which  $D$  and  $E_{at}$  are applied [7]. The energies of anion vacancy formation obtained within the extended Hückel method expectedly seem underestimated in comparison with the values calculated in the framework of other meth-

Table 7. Summarized results for the energies of vacancy formation in semiconductors

Compound	Calculation method										Literature data		
	PMX			[7]			Extended Hückel method from the Hall effect measurements			[8]			
	$E_{V_A}$	$E_{V_B}$	$E_{V_A} + E_{V_B}$	$E_{V_A}$	$E_{V_B}$	$E_{V_A} + E_{V_B}$	$E_{V_A}$	$E_{V_B}$	$E_{V_A} + E_{V_B}$	$E_{V_A} + E_{V_B}$	$E_{V_A}$	$E_{V_B}$	$E_{V_A} + E_{V_B}$
ZnS	5.65	4.33	9.98	4.96 6.49	5.17 7.65	10.13 14.14				8.49 (0 K) 9.7 (300 K)	6.05	5.71	11.76 [3]
ZnTe	4.08	2.81	6.89	3.77 4.51	5.16 6.38	8.93 10.89	4.59			8.67 (80 K) 8.27 (300 K)	4.4 4.82	4.92 5.88	9.32 [3] 10.7 [75]
CdS	5.22	4	9.22	4.28 5.81	5 6.95	9.28 12.76				7.86 (0 K) 9.03 (300 K)	5.85 6.4	4.98 5.53	10.83 [3] 11.93 [75]
CdTe				3.34 3.99	4.21 5.33	7.55 9.32		3.75*		6.16 (0 K) 7.66 (300 K)	4.38 4.81	4.38 4.81	8.76 [3] 9.62 [75]
	3.65	2.6	6.25	3.99	5.33	9.32	3.66*	3.24	6.84	7.66 (300 K)	3.44 2.67	5.66 3.24	9.1 [70] 5.91 [69]
GaAs	5.29	4.59	9.88	5.21 6.17	6.01 7.05	11.22 13.22				8.99 (0 K) 11.03 (300 K)	5.85 4.89	5.85 5.21	11.7 [75] 10.1 [67]
GaSb	5.07	4.11	9.18	5.03 5.8	5.47 6.37	10.5 12.17				9.98 (300 K)	4.99	5.52	10.51 [75]
PbTe				4.2	4.13	8.33	4.18	3.19	7.37	4.86 (0 K) 4.86 (200 K)	2.187	2.135	4.322 [74]

\* Formation energies for a once-ionized negatively charged cadmium vacancy and a twice-ionized positively charged tellurium vacancy. The formation energy for a neutral cadmium vacancy is lower than the given value by the ionization energy of the first electron, and that of tellurium vacancy formation is higher by the ionization energy of the first and second electrons [9].

ods. Moreover, provided that the method of work [7] is used in calculations, the energies of cation vacancy formation agree better with the literature data [3], if the parameter  $D$  is used; in the case of anion vacancies, it is the parameter  $E_{at}$ .

A very good correlation between the energies calculated for the metal vacancy formation and the relevant experimentally obtained data is observed for ZnTe and CdTe. A similar correlation of the experimental value for the energy of metal vacancy formation with the value calculated by the method of work [7] takes place for PbTe. For chalcogene vacancies in the CdTe and PbTe cases, this correlation is a bit worse, which is, first of all, associated with the ambiguity of its experimental determination by means of Hall measurements. When  $E$  is determined on the basis of the Hall dependences  $n_H(T, P)$ , the obtained result depends on the accepted model for the energy spectrum of defect levels in the crystal energy struc-

ture. There are several corresponding models for anion vacancies [73].

For  $A^{III}B^V$  compounds, the correlation between the calculated values is the best. Nevertheless, if the calculation method of work [7] is applied, it is more expedient to use the quantity  $E_{at}$  rather than  $D$ , as in the case of  $A^{II}B^{VI}$  compounds. While separately analyzing the thermodynamic data and the energies of vacancy formation obtained with the help of the method that is based on the application of a pair interaction potential, the following regularities should be emphasized. The application of formula (18) for the determination of the potential parameter  $a$  and the quantity  $E$  predicts a considerable growth of  $E$ , when the temperature varies from 0 to 300 K. At the same time, the values obtained for 300 K agree better with other data. On the other hand, if formula (21) is used for the determination of the parameter  $a$ , the temperature dependence  $E(T)$  is oppo-

site, and the change is much less than formula (18) predicts.

Taking all that into account, it would be of interest to calculate the enthalpies of Schottky defect formation, by using the reliable temperature dependences,  $\theta(T)$  or  $C_{ij}(T)$ . The energies of Schottky defect formation determined with the help of formula (20), i.e. on the basis of experimental values for the compression modulus, are some underestimated. However, when calculating  $B$  with the use of dependence (29), the obtained  $E$ -values agree much better with the results of calculations by formulas (18) and (21). The energies of vacancy formation obtained from the Hall data can be considered as the most probable, because they serve as a basis for the explanation of a certain experiment.

To summarize, it is worth noting that the considered empirical and semiempirical methods make it possible to evaluate the energies of defect formation. The corresponding results – for example, in the CdTe case – are not less adequate, than those obtained with the help of *ab initio* quantum chemical calculations [69, 70]. In the case of PbTe, the results obtained in the framework of the electron-density functional method [74] differ by a factor of two from those, which are used to adequately explain the high-temperature experimental results for the Hall effect, whereas the values obtained on the basis of thermochemical calculations seem to be more exact. This result gives grounds to consider the relatively simple empirical and semiempirical methods for the calculation of the vacancy formation energy, which were analyzed in this work, as an alternative, in some cases, to the resource-consuming first-principle quantum chemical methods.

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ЕНЕРГІЇ УТВОРЕННЯ ВАКАНСІЙ  
У НАПІВПРОВІДНИКАХ, ОДЕРЖАНІ  
НАПІВЕМПІРИЧНИМИ МЕТОДАМИ

Резюме

Використовуючи розширений метод Хюккеля, а також методи, що базуються на використанні термохімічних, термодинамічних та електрофізичних даних, визначено енергії утворення вакансій металу та халькогену у напівпровідникових кристалах  $A^{II}B^{VI}$ ,  $A^{III}B^V$  та  $A^{IV}B^{VI}$ . Встановлена кореляція отриманих значень як між собою, так і з літературними експериментальними та теоретичними *ab initio* даними, що свідчить про їх адекватність і можливість використання для оцінки концентрацій цих дефектів у напівпровідниках.